



Characterization of cyclopentane clathrates with gaseous guests for gas storage and separation

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HIGHLIGHTS

- Characterization of guest gas (CH₄, N₂) + CP hydrates is performed.
- CP can function as a powerful thermodynamic promoter.
- Both CH₄ and N₂ are enclathrated in sII CP hydrates.
- Guest gas enclathration does not change the structure of CP hydrates.
- Cage-specific occupation of guest molecules is observed.

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ABSTRACT

In this study, stability conditions and characterization of guest gas (CH₄ and N₂) + CP hydrates were investigated with a primary focus on phase equilibria and microscopic analyses. Four-phase (H-L_W-L_{CP}-V) equilibria of the CH₄ + CP and N₂ + CP hydrates measured at the pressure range of 0–11 MPa demonstrated that CP could significantly reduce hydrate equilibrium pressure at any given temperature and, thus, could be used as a powerful thermodynamic promoter for gas hydrates containing CH₄ and N₂. Powder X-ray diffraction revealed that guest gas (CH₄ and N₂) + CP hydrates are indexed using a cubic sII unit cell (space group *Fd3m*) and that the inclusion of guest gases does not affect the original structure of CP hydrates. It was confirmed from ¹³C NMR spectra that CH₄ molecules are enclathrated only in the small 5¹² cages of sII CH₄ + CP hydrates and that the cage occupancy of CH₄ molecules in the small 5¹² cages of sII CH₄ + CP hydrates is relatively lower than that of sI CH₄ hydrate. Time-dependent *in situ* Raman spectra also indicated the occupation of guest gases in the CP hydrate and an absence of structural transformation caused by the inclusion of guest gases. The findings of this study can broaden our understanding of cage-specific occupation of guest molecules in gas hydrates and, thus, provide important information on the application of CP hydrates to gas storage and separation.

1. Introduction

Clathrate hydrates, or gas hydrates, are non-stoichiometric inclusion compounds that can trap guest molecules in the well-defined cages built up by hydrogen-bonded water molecules [1]. Water molecules that formulate cage lattices are referred to as ‘hosts’ whereas small-sized gas or liquid molecules that are captured in the cage lattices are referred to as ‘guests’. In general, gas hydrates are thermodynamically stable under low temperatures and high pressures and exist in three distinct structures that primarily depend on the size of guest molecules: structure I (sI), structure II (sII), and structure H (sH) [1,2].

Gas hydrates have various applications in the energy and

environmental fields. The huge amount of naturally occurring gas hydrates deposited in deep ocean sediments or beneath permafrost regions is regarded as our future energy resources [1,3,4]. Gas hydrates have the capability to store 150–180 volumes of gas in a unit volume of gas hydrate and, thus, can be attractively utilized for natural gas storage and transportation [5]. Gas hydrates can also be used for CO₂ capture and sequestration. CO₂ from flue gas or fuel gas mixtures and biogas is selectively captured in the hydrate cages due to the higher thermodynamic stability of CO₂ compared to other components in the gas mixtures [6–12]. CO₂ sequestration can be combined with natural gas production by adopting CH₄-CO₂ replacement which can be used for both greenhouse gas storage and energy recovery [13–21]. Gas hydrate-

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based desalination has been also suggested for efficient water treatment [22,23]. However, the practical application of hydrate-based gas separation has been limited due to its several drawbacks such as high pressure operating condition and slow reaction rate, resulting in difficulties and a high cost for process design and operation [24].

Extensive efforts have been devoted to reduce pressure conditions required for gas hydrate formation. Various organic substances were added to gas hydrate systems to achieve thermodynamic promotion which means equilibrium pressure reduction at any given temperature [25–30]. Most thermodynamic promoters are water-miscible organic substances, such as tetrahydrofuran (THF) and 1, 4-dioxane, which are sII hydrate formers. Thermodynamic promotion by these substances is achieved through their occupation of hydrate cages and the resulting thermodynamic stabilization of the gas hydrate structure [31–37]. Cyclopentane (CP), which is water-immiscible, is another powerful thermodynamic promoter with a thermodynamic promotion capability comparable to that of THF. CP has several advantages for application to gas hydrate-based processes even though it is volatile and thus, a slight loss after repeated uses of CP would be expected [9,38–41]. CP can be easily recollected and recovered after use because it is immiscible with water and, accordingly, it shows phase separation with water after dissociation of gas hydrates.

Hydrate phase equilibrium measurements of CP hydrates with guest gases have been conducted by many researchers [39,42–45]. However, research on characterization and guest distributions of guest gas + CP hydrates has rarely been reported in the literature. In this study, CH₄ and N₂ were selected as guest gases for CP hydrates in order to examine applications of CP hydrates for gas storage and separation because CH₄ is a dominant component of natural gas and N₂ is a major component of flue gas from fossil-fuel fired power plants.

In this study, hydrate phase equilibria of CH₄ + CP + water and N₂ + CP + water systems were measured in a wide range of pressures and temperatures to examine the thermodynamic promotion effect of CP on the CH₄ and N₂ hydrates. The accurate structure of the CH₄ + CP and N₂ + CP hydrates was identified using powder X-ray diffraction (PXRD). NMR and Raman spectroscopy were used to elucidate guest distributions in the guest gas + CP hydrates and to quantify cage occupancy of guest molecules in the gas hydrate structure. In addition, the growth patterns of each guest in the pure CP and CH₄ + CP hydrates were investigated by collecting time-dependent Raman spectra using *in situ* Raman spectroscopy.

2. Experimental section

2.1. Materials and apparatus

The CH₄ with a purity of 99.95% and the N₂ with a purity of 99.99% were supplied by MS Gas Co. (Republic of Korea). CP with a purity of 98% was purchased from Sigma-Aldrich (USA). Doubly distilled deionized water was used for gas hydrate formation. All materials were used without further purification.

The specially designed high-pressure equilibrium cell was used to measure four-phase (hydrate (H) – liquid water (L_w) – liquid cyclopentane (L_{CP}) – vapor (V)) equilibria of the guest gas + CP + water systems. The equilibrium cell, which was made of 316 stainless steel and had an internal volume of 250 cm³, was immersed in a water-ethylene glycol bath that was connected to an external circulator (RW-2025G, Jeio Tech, Republic of Korea). The cell contents were vigorously mixed using an impeller-type agitator. The temperature of the cell was measured with a thermocouple which was calibrated using an ASTM 63C thermometer with an accuracy of ± 0.02 K (H-B Instrument Co., U.S.A.). The pressure of the cell was measured with a pressure transducer (S-10, WIKA, Germany), which had an accuracy of ± 0.01 MPa and was calibrated using a Heise Bourdon tube pressure gauge (CMM – 137219, Ashcroft Inc., USA).

2.2. Phase equilibrium measurement

CP is immiscible with water and, thus, the guest gas + CP + water system is univariant, indicating that CP concentrations do not affect the shift of the H-L_w-L_{CP}-V equilibrium line. However, in this study, 5.6 mol % CP solution, a stoichiometric concentration of sII hydrate, was used to measure the H-L_w-L_{CP}-V equilibria of the guest gas + CP + water systems. The equilibrium cell was filled with 60 g of CP solution (5.6 mol%) and ventilated three times with an object gas (CH₄ or N₂) to purge the residual air in the equilibrium cell. The hydrate phase equilibrium was measured under an isochoric state by controlling the cell temperature. The final equilibrium point was determined from the intersection between the hydrate dissociation line and the thermal expansion line.

2.3. XRD, NMR, and Raman analyses

To identify the accurate hydrate structure and cage-filling behaviors of guest gas + CP hydrates, the hydrate samples were analyzed using PXRD, NMR, and *in situ* Raman spectroscopy. The hydrate samples were prepared from the same reactor used for hydrate phase equilibrium measurement. After the gas hydrate formation was completed, the reactor was submerged in a liquid N₂ vessel to avoid gas hydrate dissociation and then, the vapor phase was evacuated. After pouring liquid N₂ into the reactor, the hydrate samples were taken and powered in a mortar filled with liquid N₂. For the PXRD analysis, the hydrate samples were ground into fine particles of less than 100 μm. The PXRD patterns were obtained from the 6D beamline at the Pohang Accelerator Laboratory, in the Republic of Korea. A charge-coupled device (CCD) image detector was aligned with an incident X-ray beam, and all 2θ angles were scanned. The diffraction patterns were collected with an exposure time of 60 s at 133.2 K and with an energy of 12.658 keV (λ = 0.9795 Å) after calibration of the working distance and detector orientation. The obtained two-dimensional patterns (Q-spacing, nm⁻¹) were converted into one-dimensional diffraction patterns with an energy of 8.0475 keV for comparison with the conventional PXRD patterns. The acquired PXRD patterns were analyzed using the FullProf program.

A Bruker 400 MHz solid-state NMR spectrometer at the Korea Basic Science Institute (KBSI) was used to confirm the hydrate structure and to reveal guest distributions of gas hydrates. The finely powdered hydrate samples were loaded into a 4 mm o.d. Zr-rotor and analyzed at 243 K. The ¹³C NMR spectra were collected at a Larmor frequency of 100.6 MHz with a magic angle spinning (MAS) of 2–4 kHz. The downfield carbon resonance peak of adamantane (38.3 ppm at 300 K) was used as an external chemical shift reference.

An *in situ* Raman spectrometer (SP550, Horiba, France) with a multichannel air cooled CCD detector and a 1800 groove/mm grating was used to observe the enclathration and growth behavior of each guest during hydrate formation and to confirm the structural change of guest gas + CP hydrates. Time-dependent Raman spectra during gas hydrate formation were collected using a fiber-optic Raman probe attached to the jacketed reactor. The subcooling temperature (ΔT), which is defined as the difference between the equilibrium temperature and the experimental temperature at a given pressure, was set to 5.0 K for CP hydrate formation under atmospheric pressure and 5.0 K for CH₄ + CP hydrate formation at 4.0 MPa. The pressure was maintained during hydrate formation using the constant pressure mode of a syringe pump (ISCO 500D, Teledyne, USA). More detailed description for experimental apparatus and procedure were given in our previous papers [8–10,13–15].

3. Results and discussion

Thermodynamic studies of guest gas + additive + water systems, especially hydrate phase equilibria, are very important in predicting

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